Metallurgy and Foundry Engineering – Vol. 39, 2013, No. 1, pp. 39÷45
http://dx.doi.org/10.7494/mafe.2013.39.1.39

Grzegorz Boczkal
Małgorzata Perek-Nowak

STRUCTURE AND ELECTRICAL PROPERTIES OF Sn8Zn SOLDER ALLOY WITH Ag AND Ga ADDITIONS

STRUKTURA I WŁAŚCIWOŚCI ELEKTRYCZNE STOPÓW LUTOWNICZYCH Sn8Zn Z DODATKIEM Ag I Ga

Abstract

Solder joints based on eutectic SnZn alloy were studied. The influence of Ga and Ag was analysed and compared to the basic Sn8Zn alloy as well as to the reference solder alloys Sn60Pb40 and Sn3Cu. The formation of intermetallic layer in zinc-containing alloys made mainly out of Cu5Zn8 type was noted, while in the standard solder alloys it was Cu3Sn. The resistivity measurements showed the lowest value for Sn8Zn1Ag and the worst in the case of Sn8Zn1Ga, due to the quite different incorporation of Ag and Ga atoms in the solder: Ag atoms are found in precipitates while Ga atoms are dissolved in the matrix.

Key words: *lead-free solders, intermetallic phase, resistivity measurements*

Streszczenie

W pracy przedstawiono badania dotyczące połączeń lutowanych na bazie stopu eutektycznego SnZn. Porównano wpływ dodatków stopowych Ga i Ag w stosunku do referencyjnego stopu Sn8Zn i stopów lutowniczych Sn60Pb40 i Sn3Cu. Zauważono wytworzenie warstwy międzymetalicznej w stopach zawierających cynk, która zbudowana była głównie ze związku typu Cu5Zn8, podczas gdy w standardowych stopach jest to zwykle faza Cu3Sn. Badania oporności wykazały najniższą wartość dla stopu Sn8ZnAg, a najwyższą dla stopu Sn8ZnGa, ze względu na różny sposób rozmieszczenia atomów Ag i Ga w połączeniu lutowanym: atomy Ag znajdują się w wydzieleniach, a Ga są rozpuszczone w osnowie.

Słowa kluczowe: *luty bezołowiowe, faza intermetaliczna, pomiar oporności*

Grzegorz Boczkal Ph.D. D.Sc., Małgorzata Perek-Nowak Ph.D., AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Krakow, Poland; gboczkal@agh.edu.pl

1. Introduction

An intermetallic phase and growth of an interface influence efficiency and reliability of solder joints. The application of Sn-Pb alloys into copper-based connections causes the formation of the Cu_6Sn_5 and Cu_3Sn compounds. The increased growth of the intermetallic layers of CuSn decreases thermal endurance, tensile strength and brittle fracture of the solder joint. The electronic industry experienced great development in the field of introducing lead-free solders. Currently, the most popular lead-free solder is a triple nearly-eutectic Sn-Ag-Cu (SAC) alloy [1, 2]. The intermetallic compounds, which form between the SAC and copper base are similar to those found in the Sn-Pb/Cu connections. Also some studies are reported on intermetallic phases found in the Sn-Cu solder joints [3] and Sn-Ag [1, 4, 5]. Besides, various additions to the Sn-Ag alloy such as Ni, Cu, Al, Zn, Co, Sb, P and Au were studied in [6] and the interface layer is similar to that found in SnZn with additions.

Therefore, the eutectic alloy Sn-Zn was taken into consideration as a lead-free solder, due to its low melting temperature, excellent mechanical properties and low costs. Its microstructure is characterized by coarse grains with fine, uniform two-phase eutectic precipitates. Due to the large concentration of alloying components such as zinc, the alloy is less susceptible to whisker formation.

2. Experimental method

The samples were prepared from a sheet of 99,995 wt.% copper and the following soldering alloys: Sn3.5Zn, Sn8Zn, Sn8Zn1Ag, Sn8Zn1Ga, Sn3Cu and Sn60Pb40. The thickness of the sheet was 2 mm. The soldering alloys Sn3Cu and SnPb, and the flux agent are standard alloys used here for reference. All the samples were prepared using the flux agent dedicated for copper soldering.

The studied alloys Sn3.5Zn, Sn8Zn, Sn8Zn1Ag, Sn8Zn1Ga were produced by melting necessary elements together. All the pure materials were weighted previously on a precise laboratory scale. The purity of the materials was as follows: 99,99 wt.% Sn, 99,995 wt.% Zn, 99.99 wt.% Ag and the 99.99 wt.% Ga. Metals were melted in graphite crucibles and cast into a flat form, which were then rolled to a thickness of 0.5 mm.

The copper sheet of thickness of 2 mm was cut into plates of dimensions of 40×50 mm. Next, the plates were cut on the length of 30 mm with a precise saw, what guaranteed identical width of the soldering slit of 0.5 mm. The rolled alloys together with the flux agent were put in sequence in the slits and soldered in a furnace chamber at a temperature of $250^{\circ}C$ for 20 min in the argon atmosphere. The furnace was specially designed for the soldering process of the samples (Fig. 1). Due to electrical heating the minimal temperature gradient was ensured. The power of a transformer was chosen n such a way that the furnace was heated to the required temperature. After the soldering process, the copper winding of a tubular radiator allowed for fast cooling of the samples to the ambient temperature. Inside the furnace, samples were placed on a ceramic table at the height of heating elements. A thermocouple was used to control the temperature. Observations of a sample was possible through glass windows on the sides of the furnace. After removal from the furnace, all samples were polished using sand paper. Next, the samples were cut into smaller pieces 4 mm wide and 40 mm long with solder in the middle. These were the final samples for studies of electrical resistance.

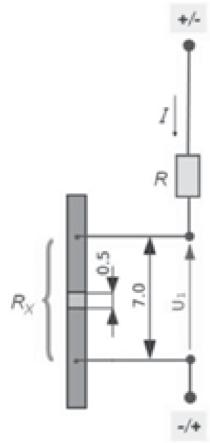

Fig. 1. Scheme of four-point method of resistivity measurements

The samples for scanning electron microscopy observations were additionally polished at cloth with 1 μm diamond paste. The analyses were performed at SEM (scanning electron microscope) Hitachi S-3400N with a tungsten electron gun and accelerating voltage of 20 kV. The analyses of the chemical composition of the phases present within the joint were performed by means of the EDS (Electron Depressive Spectrometry) method at the Noran attachment to the mentioned SEM.

The resistance studies were conducted by a four-point method at a holder equipped with contactors in the form of gold-plated needles of beryllium bronze. Springs pressed against the needles to the samples to decrease the influence of thermal contraction during testing in liquid nitrogen. To measure the voltage, two precise digital multimeters HP 3458A and Agilent 34401A with a resolution of 10 nV and 100 nV, respectively, were used. The scheme of the measuring system is presented in Figure 1, where R_x is resistivity measured between two contactors separated by a distance of 7 mm, and U is the measured voltage. The voltage was supplied from the stabilized current supply. The specimens were submerged into liquid nitrogen for testing in order to reduce the thermal component. Thirty separate measurements were conducted on each sample, where the polarization of the current was inverted every time. The time interval between individual measurements was 2 s.

3. Discussion

3.1. Structural analysis

The Sn8Zn alloy used as a basic soldering alloy has eutectic composition, which melts at 198^{O}C. The melting temperature of SnZn is in between the typically applied soldering alloys Sn60Pb40 (183^{O}C) and Sn96Ag4 (221^{O}C). A small concentration of Ga and Ag atoms (only 1 wt.%) were added into the alloy to study their influence on the development of the solder/metal interface. The two elements exhibit completely different behavior in the alloys: Ga remains in an alloy matrix, while Ag forms precipitates. Additionally, silver refines the structure and the eutectic phase is much finer and Ga decreases the eutectic temperature and surface tension of the solder/copper system.

The interface solder/metal sheet varies with the concentration of zinc and with alloying additions from flat to irregular. The smoothest interface is observed between Sn8Zn solder and copper sheet. The interface is quite smooth on the whole length with thickness of about 25 μm (Fig. 2c). The composition of the intermediate layer (point 1, Fig. 2c) is given in Table 1 where it is indicated that the phase is made of Cu5Zn8-type intermetallic phase. Similarly, the shape of the interface found in the specimen soldered with Sn8Zn1Ag alloy is quite flat with thickness of about 20 μm, however the border from the solder side is slightly serrated (Fig. 2b).

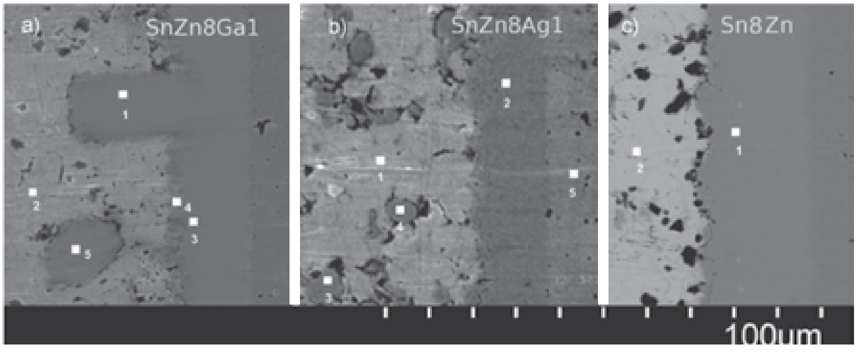

Fig. 2. SEM micrograph of interface: a) Sn8Zn/Cu, b) Sn8Zn1Ag/Cu, c) Sn8Zn1Ga/Cu with marked points of EDS analysis; chemical composition of the phases at respective points is given in Table 1

Table 1. Chemical composition of solder alloys, at.%

Solder alloy	Al-K	Cu-K	Zn-K	Ag-L	Ga-K	Sn-L
Sn3Cu(1)_pt1	0.68	54.78	—	—	—	44.54
Sn3Cu(1)_pt2	0.50	74.85	—	—	—	24.65
Sn3Cu(1)_pt3	1.01	2.92	—	—	—	96.07
Sn3,5Zn_pt2	1.19	3.18	—	—	—	95.63
Sn3,5Zn_pt3	0.64	55.55	6.41	—	—	37.41
Sn3,5Zn_pt4	0.68	56.35	5.80	—	—	37.16
Sn8Zn_pt1	0.58	35.05	64.37	—	—	—
Sn8Zn_pt2	0.93	2.63	—	—	—	96.44
SnZnGa_pt1	—	36.55	61.87	—	0.62	—
SnZnGa_pt2	—	3.61	10.00	—	1.58	83.81
SnZnGa_pt3	—	15.50	25.88	—	0.49	—
SnZnGa_pt4	—	31.51	58.22	—	1.21	8.31
SnZnGa_pt5	—	34.52	63.14	—	0.99	—
SnZnAg_pt1	—	—	—	—	—	100.00
SnZnAg_pt2	0.40	34.17	64.49	0.94	—	—
SnZnAg_pt3	0.76	31.37	65.14	2.73	—	—
SnZnAg_pt4	0.60	29.34	66.86	3.20	—	—
SnZnAg_pt5	0.49	99.51	—	—	—	—

The composition of all phases formed is given in Table 1, what indicates that the interface is formed mainly from Sn and Zn (Cu5Zn8-type phase) with a slight addition of silver. Additionally, areas of similar compound however enriched in silver are formed inside a solder (points 3 and 4, Fig. 2b). Also the composition of the continuous interface layer thick for about 20 μm is similar to that in the sample joined by the Sn8Zn alloy (point 1 in Fig. 2c and point 2 in Fig. 2b), about 64 at.% Zn and about 35 at.% Cu.

On the contrary, the interface in the rest of the studied solder alloys including the reference alloy Sn60Pb40 is coarse (Figs. 3, 4). The differences, however, are clearly visible in the Figures 2a, 3 and 4a, 4b. The joint performed with the use of Sn8Zn1Ga alloy is rather flat similar to the case of the Sn8Zn alloy with the tongues rectangular in the cross-section (Fig. 2a). The 'basic' layer is flat on the copper side and slightly serrated on the solder side with thickness of about 20 μm. However, the tongues may grow even up to 42 μm. Some islands of precipitates are formed inside the solder. The EDS analysis of the interface showed quite different results from the previously discussed ones as it does not contain any tin atoms within (points 1 and 3, Fig. 2a). The tin remains completely within the solder (points 2, Fig. 2a) and about 8% in the narrow layer between the intermetallic phase and the solder (point 4, Fig. 2a). Gallium atoms move to the interface, however most stay in the solder alloy (points 1 to 5, Fig. 2a). Considering the results from Table 1 and the Zn-Cu phase diagram [7], the interphase can be determined to be Cu5Zn8.

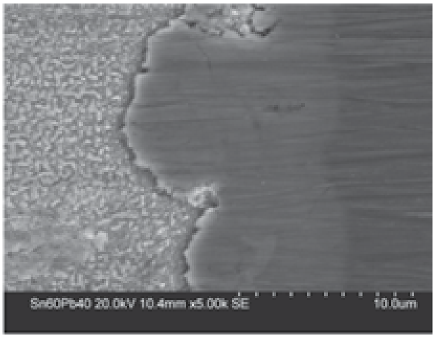

Fig. 3. SEM micrograph of interface Sn60Pb40/Cu

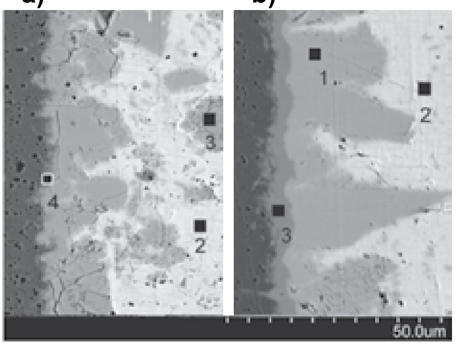

Fig. 4. SEM micrograph of interface: a) Sn3.5Zn/Cu, b) Sn3Cu/Cu, chemical composition of the phases at respective points is given in Table 1

The connection Sn3.5Zn/Cu is coarse on both sides of the interface, however, the solder side is more developed than the copper side (Fig. 4a). The thickness of the intermetallic layer varies from 7.74 to 29 μm. Moreover, some precipitates within the solder are much larger than in the case of Sn8Zn1Ag, even over 22 μm. The chemical composition of the layer and precipitates is alike (points 3 and 4, Fig. 4a), about 55 at.% Cu, 37 at.% Sn and 6% at.% Zn, as shown in Table 1. There is no additional layer observed at the interface as it will be discussed later in the case of the samples soldered with Sn3Cu alloy (Fig. 4b).

It is worth noting that the phase formed in the sample soldered with Sn3.5Zn is quite brittle both in the interface layer as well as in the large precipitate inside solder (point 3, Fig. 4a).

The specimen joined with the Sn3Cu alloy next to the very coarse structure exhibits the formation of an additional layer of thickness of about 5 μm (Fig. 4b). The composition of this narrow layer is given in Table 1 at point 2. It differs considerably from the composition of the larger, irregular layer by a bigger content of copper (point 1, Fig. 4b). Thus, the thin layer is made out of the Cu_3Sn intermetallic phase, while the larger layer is Cu_6Sn_5. The thicker layer may grow to about 40 μm into the solder alloy. The rest of the joint is made of the original alloy Sn3Cu as indicated in Table 1 for point 3.

3.2. Resistivity measurements

The resistivity measurements were performed by the four-point method in the liquid nitrogen bath. All analyzed alloys exhibit similar electric properties. Studies conducted at liquid nitrogen temperature showed that the smallest resistance has connection made of Sn8Zn1Ag alloy (Fig. 5). The microstructural analysis showed high homogeneity of the interface made of Sn6Zn5 phase. Moreover, regions reach in Ag were observed within the solder. The homogeneous structure of the interface may translate to better conductivity of the connection and good repeatability of joints at industrial conditions.

On the other hand, the alloy with 1% of Ga content presents the worst conductive properties due to the highly unhomogeneous interface. The addition of Ga atoms improved diffusion parameters in the alloy by decrease of melting temperature of the eutectic and change of thermodynamic potentials of the system.

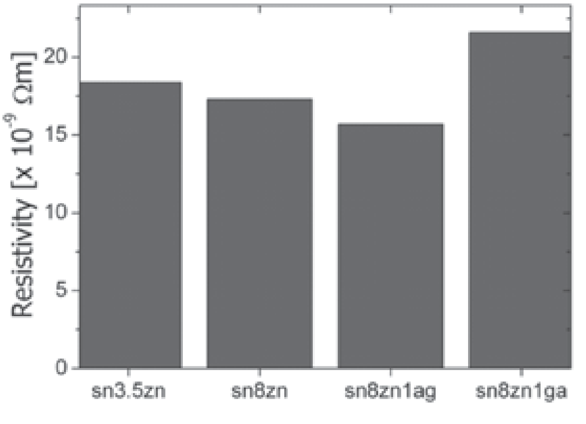

Fig. 5. Resistivity of solder joints

4. Conclusions

Based on the results it can be concluded that:

– the width of the diffusion layer at the interface is comparable for all alloys with concentration of zinc equal to 8% (25 μm for Sn8Zn, 20 μm for Sn8Zn1Ag and Sn8Zn1Ga).
– at the concentration of zinc above 3.5%, a smooth and regular brass layer forms at the interface, which limits the formation of the Sn_6Zn_5 phase. The layer decreases stresses in the solder and may also decrease susceptibility to the formation of whiskers.
– the shape of the interface in the case of Sn3.5Zn is very irregular while the Sn8Zn alloy and its modifications form connections with the smooth and regular interface.
– in the case of the Sn8ZnAg alloy, the formation of the following phases: Cu_5Zn_8, and regions of higher Ag (about 2 at. %) content were observed. The interface was made of CuZn compounds, while the phases containing silver were found inside the solder.
– the increase of zinc concentration in the alloy from 3.5% to 8.0% changes slightly the value of the resistivity. The addition of gallium increases the resistivity of the alloy while the increase of silver by few percent improves the resistivity of the solder.

References

[1] Kang S.K., Choi W.K.: Journal of Electronic Materials, Vol. 31 (2002) pp. 1292–1303
[2] Islam M.N., Chan Y.C., Rizvi M.J., Jillek W., Journal of Alloys and Compounds, Vol. 400 (2005) pp. 136–144
[3] Shin C.K., Baik Y.-J., Huh J.Y., Journal of Electronic Materials, Vol. 30 (2001) pp. 1323–1331
[4] Boczkal G., Marecki P., Perek-Nowak M., Archives of Metallurgy and Materials, Vol. 57 (2012) pp. 33–37
[5] Sigelko J., Choi S., Subramanian K.N., Lucas J.P., Bieler T.R., Journal of Electronic Materials, Vol. 28 (1999) pp. 1184–1188
[6] Amagai M., Microelectronics Reliability, Vol. 48 (2008) pp. 1–16
[7] Massalski T. B., Editor-in-Chief; H. Okamoto, P. R. Subramanian, L. Kacprzak, Editors. ASM International, Materials Park, Ohio, USA, (1990)